Green Multifunctional Organic-Inorganic Hybrids based on Biopolymers and Recyclable materials

Sidney J.L. Ribeiro
Institute of Chemistry
São Paulo State University -UNESP
Araraquara, São Paulo
Brazil
sidney@iq.unesp.br
University of the State of São Paulo
UNESP

32 schools / 23 cities

169 undergraduate programs

35,000 undergraduate students

10,000 graduate students

9,000 Diplomas per year

3,400 Academic staff (95% PhDs – 87% full time)

7,000 Non academic staff
ARARAQUARA
“City of the Sunshine”
“World capital of oranges”

~200,000 inhabitants
18th in São Paulo
1st in quality of life
Undergraduate and Graduate Chemistry Studies
80 prof/res, 1000 undergraduated students, 500 graduated students (>1000 theses)
Laboratory of Photonic Materials

Sidney J.L. Ribeiro
Full Professor, Researcher Class 1A CNPq
Member of the Academy of Sciences of the State of SP

Younes Messaddeq
On leave from UNESP
Canada Excellence Research Chair
PhD- Univ. Rennes- France

7 pos-docs, 10 grad- std, 10 undergrad. std

Development of novel photonic materials

Education  Health  Agriculture  Environment  Telecom

Technology Transfer  Science dissemination
Photonics - photons as information carriers

Photophone
1880

- Lasers
- Optical fibers
- Efficient detectors
- modulators
- Optical fibers

electronics  Opto-electronics  Photonics

20th century  21th century

"There is something wrong with my cell phone...
...it doesn't have your number in it.”
- Alexander Graham Bell
Materials for Photonics

How new are the “state of the art materials” we are using?

Lycurgus cup
"the most spectacular glass of the period, fittingly decorated, which we know to have existed"

Roman and Venetian Glasses
Au/Ag nanoparticles

Absorption and scattering effects in the control of the colors we see

Can we control the light by using metal NP´s in order to enhance Si solar cells efficiency??
Materials for Photonics
How new are the “state of the art” materials we are using?

1st Organic-Inorganic Hybrid
(indigo blue dye + clays)

Amazing resistance to weathering
over more than 15 centuries!!!

Maya blue
8th to 15th centuries

Can we enhance resistance to weathering of
organic devices (OLEDs, solar cells, etc??)

We still don’t know how Maya artists prepared their blue pigment!!
Summary

Down-conversion

Up-conversion

Graph showing spectral irradiance and maximum fraction available for DC and UC.
Green materials for Photonics

Butterflies
Optical properties

Cellulose from Bacteria
Gluconacetobacter xylinus

Silk based materials
Bombix mori
Can we enhance the efficiency of Si photovoltaic cells?
Upconversion and anti-Stokes Process with f and d ions in Solids

François Auzel

**Figure 3.** Various two-photon upconversion processes with their relative efficiency in considered materials.
Up-conversion

Si

Up-converter

mirror

ΔE, cm⁻¹

25
20
15
10
5
0

Er³⁺

²H(G)⁹/²
⁴F₅/², ⁴F₅/₂
⁴F₇/₂
⁴S₅/₂
⁻I₉/₂
⁻I₉/₂
⁻I₁₁/₂
⁻I₁₃/₂
⁻I₁₅/₂

550 nm
660 nm
980 nm

Irradiance W m⁻² nm

0
1,0
1,4
1,6

section efficace*10² cm²

Longueur d'onde (nm)
Surface plasmons from metal NP’s can enhance luminescence (similar to SERS)

Large Enhancement of Upconversion Luminescence of NaYF₄:Yb³⁺/Er³⁺ Nanocrystal by 3D Plasmonic Nano-Antennas

Weihua Zhang, Fei Ding, and Stephen Y. Chou*

Figure 3. Enhanced upconversion luminescence on the optimized D2PA substrate. (a) Upconversion luminescence spectra on both the D2PA and reference substrates. Photoluminescence photography of NaYF₄:Yb³⁺/Er³⁺ nanocrystals at 530 nm (b), 660 nm (c) on the D2PA substrate, and on the reference substrate (d) measured at the same condition. The scale bar is 100 μm.
Figure 1: Scheme of the structure; the up-converter layer is placed between a gold layer (mirror) and periodic arrays.

Figure 7: Determination of the total enhancement factor of structures, with a layer deposited on glass substrate as reference.
Down-conversion or Quantum Cutting
2 IR emitted photons for 1 UV-VIS absorbed photon
200% quantum yield
Fluoride Glasses- Low phonon glasses
Two important optical properties governed by the phonon energy of the host:

Multiphonon edge in glass:

\[ \omega_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]
\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

Non-radiative decay

Lanthanide ions:
Weak coupling regime and non-radiative decay occurs through multi-phonon relaxation

Fluoroindate glasses $\text{InF}_3-\text{BaF}_2-\text{SrF}_2-\text{ZnF}_2$

Pr$^{3+}$-Yb$^{3+}$

NRD are lower in low-phonon hosts
Silica- 1100 cm$^{-1}$
Fluorides- 500-600 cm$^{-1}$
Pr$^{3+}$ emission as a function of [Yb$^{3+}$]

Energy transfer Pr$^{3+}$ → Yb$^{3+}$
Pr\textsuperscript{3+} decay time as a function of [Yb\textsuperscript{3+}]

\[ \lambda_{\text{exc}} = 453.5 \text{ nm} \]
\[ \lambda_{\text{obs}} = 604 \text{ nm} \]

Energy transfer Pr\textsuperscript{3+} \rightarrow Yb\textsuperscript{3+}
IR emission

Energy transfer $\text{Pr}^{3+} \rightarrow \text{Yb}^{3+}$
Front face illumination

Rear illumination
Bragg diffraction of visible light
PHOTONIC CRYSTALS
Energy & Environmental Science

Cite this: Energy Environ. Sci., 2012, 5, 9195

www.rsc.org/ees

**REVIEW**

**Butterflies: inspiration for solar cells and sunlight water-splitting catalysts**

Shuai Lou,† Xingmei Guo,† Tongxiang Fan* and Di Zhang
Solar Cells and photocatalysts to yield hydrogen

Significant strategies for utilizing clean and sustainable solar energy to replace conventional fossil fuels.

Light manipulation and harvesting abilities play a dominant role in the conversion efficiencies.

Butterflies inspiring new solar cells and sunlight water-splitting catalysts

Nipple arrays in butterfly compound eyes
Ridge and hole arrays
Photonic crystal structures in butterfly wings
Table 1 Typical optical architectures in butterflies exhibiting different effects and corresponding potential applications for clean energy

<table>
<thead>
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<td>Sawtooth type with air gaps</td>
<td>Argyrophorus argenticeps</td>
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<td>Bead array</td>
<td>Pierid butterflies</td>
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Fig. 12 (a) Optical photograph of facet lens on the compound eye of butterfly Euploea mulciber. (b) SEM image of the facet lens on the compound eye. (c) SEM image of nipple arrays on the borders between facet lens. (d) Detail, showing the local arrangement of domains with highly ordered nipple arrays. Scale bars, (a) 10 μm, (b) 20 μm, (c) 2 μm, and (d) 200 nm. Provided by T. X. Fan, Shanghai Jiaotong University.

Fig. 13 Schematic diagram of the process steps for the fabrication of parabola-shaped SWG structures on an AZO film/Si substrate. Reprinted from ref. 68.

SWG- subwavelength gratings
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<td><strong>Papilio zalmoxis and Papilio nius</strong></td>
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<td>Papilionids and lycanids</td>
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![Fig. 16](image) Structure and model of butterfly *Ornithoptera goliath*. (a) An overall view of the butterfly. (b) Optical microscopic image of the scales of the black area. (c) FESEM image of the microstructures of the scales. (d) and (e) Cross-sectional views of a single scale with parameters for modelling. (f) Schematic diagram showing the overlapped area of the scales. (g) Dimensions of 3D FDTD model. (a): distance between two ridges; (b): height of the ridges; (c): distance between the bottom of the ridge and the base slab; (d): thickness of the base slab; (e): half vertex angle of the ridge; (f): thickness of the ridge wall. (h) Schematic diagram in constructing the planar scale model by squeezing the 3D original model into a slab of the same bottom area and volume. Scale bars: (a) 2 cm, (b) 50 μm, (c) and (d) 2 μm, (e) 1 μm. Reprinted from ref. 72.

![Fig. 15](image) Schematic diagrams of imprinting process for solar cell structure. Reprinted from ref. 71.
Table 1  Typical optical architectures in butterflies exhibiting different effects and corresponding potential applications for clean energy

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Fig. 25  (a) Optical microscope image of a green scale from the butterfly *Papilio nivias.* (b) Scanning electron microscope image of the PCS in the *P. nivias* colored scale showing fractured air cylinder edges. (c) Transmission electron microscope image of a section through a *P. nivias* colored scale, taken at a small angle to the plane of the PCS. (d) Band diagram of *P. nivias* intradomain PCS structure (the horizontal bar at 505 nm represents fluorescence emission full width at half maximum). Scale bars: (a) 50 μm, (b) and (c) 1 μm. Reprinted from ref. 57.

Fig. 26  (a) Schematic of the cell fabrication process. (1) Formation of the PC layer. (2) Further formation of the NT layer. (3) Detached bi-layer was detached from the Ti substrate. (4) The detached bi-layer was glued to a fluorine doped tin oxide (FTO) substrate with TiO₂ nanoparticles. (5) Final assembly of the DSSC. (b) Cross-section image of the fabricated PC layer. Inset: the PC layer transferred onto a FTO substrate showing a green color. (c) Photographs of PC samples (in ethanol) of various colors. Scale bar: (b) 1 μm. Reprinted from ref. 81.
Cellulose produced by bacteria
Cellulose

Most abundant polymer on earth;

Fantastic rich chemistry

All requirements from "green" approaches;

Excellent perspective for new "green polymers";
Cellulose is:
scientifically interesting,
eco-friendly material,
green,
biocompatible,
obtained from renewable sources,
recyclable...

BUT, YOU NEED TO BE
FAR, FAR, AWAY
FROM
THE CELLULOSE PRODUCTION PLANT!!!
International Conflict - since 2006 in International Court, The Hague

Where to install a cellulose plant??
http://en.wikipedia.org/wiki/Pulp_mill_dispute

The problem

“Potentially negative environmental, social, and economic impacts that the installation of cellulose plants on the margins of the Uruguay River can have for the local residents of the area involved”

28 July 2011
binational commission CARU (Spanish: Comisión Administradora del Río Uruguay) monitoring the river pollution - official end of the dispute
Fortunately, plants are not the only cellulose source available...
Gluconacetobacter xylinus

BACTERIAL CELLULOSE or BIOCELLULOSE

Bacterial cellulose (biocellulose) hydrogel
- high mechanical resistance
- 98% water - 2% pure cellulose
- 3D nanometric network
- open structure, easy to functionalize
Biocellulose

The nanometric structure leads to better chemical and mechanical properties

BC fibrils - (1/100) of those from plants cellulose
W^{6+} \rightarrow W^{5+}

Phosphotungstic acid - PWA

chiral nematic phase

cellulose reflective films
Bombix mori
SILK PRODUCERS
Bombyx mori
"Silk spinners"

mulberry

Fibroin-based optical materials
"Silk Bio-Optronics"

Bombyx mori
"Silk spinners"

protein-based materials

"Reverse engineering"
Japanese immigration to Brazil - 1920's

"Silk valley"

Biggest production in the Occident
In the world - 3rd place (after China and India)
SILK = FIBROIN + SERICIN

- **Sericin**: glue-like protein
- **Fibroin**: fibrous protein composed of β-sheets

*Images:*
- Silk cocoon
- Silk yarn
Fibroin solution

extraction of sericin

Na₂CO₃

Fibroin dissolution

CaCl₂

8%wt
50% yield

2 days

dialysis

Magnetic sponges

[fibroin]

T
Superparamagnetic maghemite nanoparticles

Coprecipitation method

\[ 2\text{Fe}^3+(aq) + \text{Fe}^2+(aq) + 8\text{OH}^-(aq) \rightarrow \text{Fe}_3\text{O}_4(s) + 4\text{H}_2\text{O}(l) \]

- FeO.\text{Fe}_2\text{O}_3
- Magnetite or Iron Ferrite
- Inverse spinel fcc structure

\[ \text{Fe}_3\text{O}_4(s) \underset{O_2}{\rightarrow} \gamma^{-} \]

\[ \gamma^{-}\text{Fe}_2\text{O}_3 \]

Maghemite
- Inverse spinel fcc structure

Ionic Ferrofluid
- Colloidal stability by oleic acid
Silk Ferrogels

"magnetic squeezing"

M.Zrinyi et al., Polymer Gels and Networks (1997) 5, 415

Silk Fibroin Solution

Maghemita

$\gamma$-Fe$_2$O$_3$
Luminescent diffraction gratings

Silk replicas

Master
(commercial DVD)

Track Pitch - CD: 0.740 μm  DVD: 1.6 μm

Fibroin solution + Eu³⁺ complex or Rhodamine 6G poured onto the master and dried

Luminescent silk replica
Eu$^{3+}$ emission

UV pointer laser

Green pointer laser
Conventional laser

Spontaneous emission

Stimulated emission

1916 - Einstein

1958 Schawlow – Townes
1960 Maiman

Cavity modes
Narrow linewidth

Long coherence time

Large spatial coherence

Directionality

beam profile  speckle
Laser paint – Random lasers


Rhodamine with TiO$_2$ nanoparticles

Multiple scattering inside the cell - stimulated emission

Random Laser

“laser paint” or “photon bomb”

Large linewidth
Short coherence time
Small spatial coherence

NO speckle

Cid Araujo - Recife - Brazil
Random lasers- a new kind of light source for imaging. High photon degeneracy/spectral radiance and low spatial coherence

It is the ideal combination for full-field imaging

Random lasers produce speckle-free images

It is the ideal combination for full-field imaging.

Random lasers produce speckle-free images.
DFB (Distributed Feedback) or DBR (Distributed Bragg Reflector)

http://www.cstf.kyushu-u.ac.jp/~adachilab/images/dfb.jpg
DFB + Random lasers

Fibroin Bragg gratings doped with rhodamine 6G

Silica (Stober) particles (scatterers)
DFB-Random lasers

(a)
F.G. Omenetto, D.L. Kaplan
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- Hermi F. Brito, Maria Cláudia F. C. Felinto- São Paulo
- Marcos Antonio Couto dos Santos- Aracajú
- Luiz A. O. Nunes- São Carlos

Nanobiotec
Capes, Brazil
PhD and Pos-Doc positions available

sidney@iq.unesp.br
Castor Oil- a multifunctional “green precursor” in materials science

Castor oil
Ricinus Communis ("Castor plant")
90% of hydroxy, unsaturated C\textsubscript{18} fatty acid

Polymers, cosmetics, coatings, resins, biodiesel…
ORGANIC-INORGANIC HYBRIDS

Organic counterpart

Inorganic counterpart

Hybrids Materials
Composites at the molecular scale

Amidosil
Synthesis of the monoamidosil precursor

\[
\begin{align*}
\text{Ricinoleic acid} & \quad \text{APTS} \\
\text{THF} & \quad 80^\circ
\end{align*}
\]
Water (hydrolysis and condensation)

Amide formation confirmed by FTIR and NMR

Amidosil hybrid
Eu$^{3+}$ compounds


By Luís D. Carlos,* Rute A. S. Ferreira, Verónica de Zea Bermudez, and Sidney J. L. Ribeiro

Strong red light emitters under excitation of light, high energy radiation, electric field, mechanical stress, etc.

The spectroscopic study allows one to obtain important information on the structure and nature of the host

Luminescent materials
Lasers, optical amplifiers,
Labels for imaging and diagnostics sensors, etc

Structural probe for:
-new amorphous or crystalline hosts
-compounds of spectroscopically inert ions like Ca$^{2+}$
Luminescence excitation

**ff transitions** - low absorption coefficient \((\varepsilon \sim 10)\)

**dd transitions** - \(\varepsilon \sim 1000\)

**organic molecules** - \(\varepsilon \sim 10^6\)

Enhancement of the light absorption efficiency, followed by energy transfer to \(\text{Eu}^{3+}\), and enhancement of the light output.
Sample under UV illumination

\[ \text{tta-} \]

\[ [\text{Eu(tta)}_3(\text{H}_2\text{O})_2] + \text{tta-} \]
Luminescence

Pure hybrid
Broad band shifting with the excitation wavelength
Electron-hole recombinations
$[\text{Eu(TTA)}_3(\text{H}_2\text{O})_2]$}

Emission

Excitation

$\lambda_{\text{exc}} = 350\text{nm}$

$\lambda_{\text{em}} = 612\text{nm}$

$^5\text{D}_0$ quantum efficiency:

$\left(\frac{\tau_{\text{EXP}}}{\tau_{\text{RAD}}}\right) = 22\%$

$^7\text{F}_j$

$k_{\text{RAD}}$

$k_{\text{NRAD}}$ - non-radiative
Amidosil+[Eu(TTA)$_3$(H$_2$O)$_2$]

Excitation- Antenna effect enhanced in the amidosil host
(water molecules are substituted by functional groups from the host)
Amidosil+\([\text{Eu(TTA)}_3\text{(H}_2\text{O)}_2]\)
PhD and Pos-Doc positions available

sidney@iq.unesp.br
Fig. 33  Hydrogen evolution of the samples in 10% aqueous methanol under UV and visible light irradiation. (a) Comparison between ABWA TiO$_2$ and NT TiO$_2$. (b) Comparison between ABWA TiO$_2$ series loaded with different amount of Pt particles. Reprinted from ref. 95.